

**TRIBOLOGY STUDY ON NANOSILICA-FILLED  
POLYURETHANE (PU) COMPOSITE COATING ON  
POLYPROPYLENE SUBSTRATE**

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## ABSTRACT

Acrylic based polyurethane coatings with nanoparticles embedded were prepared. The effects of nanoparticles of silica as fillers in the epoxy composite systems on tribological properties have been discussed in this article. The dispersed of nanosilica in polyurethane solution were prepared under magnetic stirring and various amounts of nanosilica powders were added so that the amount would turn out to be 3, 7 and 10% by weight respectively. The reference control was a pure polyurethane film with no nano silica content. The tribological tests were carried out by sliding against stainless steel in a pin on plate contact mode for friction and wear tester under a dry and clean condition. The sliding performs at rotary speed of 100 rpm and 200 rpm with 0.1kg to 0.4kg load with 0.1N interval, sliding for 10 minutes time. The effect of coating composition on friction and wear behaviour of composite coatings and the worn surface after testing then was observed by using optical microscope. The coating film seemed to be continuous and homogeneous since no agglomerates occur. Lower and optimum content of 3.0 wt% nanoSiO<sub>2</sub> filled PU give the lowest friction and wear rate when the applied load and speed were increased.

**Keywords** : acrylic based polyurethane, nanocomposite coating, friction and wear behaviour

## ABSTRAK

Salutan poliuretana yang berasaskan akrilik dengan menggunakan nanosilika sebagai partikel terbenam telah disediakan. Kesan nanopartikel silika sebagai pengisi di dalam salutan epoksi komposit ke atas sifat tribologi telah dibincangkan di dalam artikel ini. Nanosilika terserak ke dalam larutan poliuretana telah disediakan dengan menggunakan pengacau magnetik dan pelbagai jumlah kandungan nanosilika telah ditambah untuk menjadikan larutan mempunyai 3, 7 dan 10% mengikut jumlah berat masing-masing. Satu larutan poliuretana tanpa kandungan nanosilika telah disediakan sebagai rujukan kawalan. Ujian tribologi telah dijalankan dengan menggelongsorkan sampel dengan keluli tahan karat dengan menggunakan pin dengan plat mod untuk menghasilkan kesan geseran dan haus dalam keadaan kering dan bersih. Proses penggelosoran telah dilakukan dengan kelajuan bersaling 100 rpm dan 200 rpm dengan beban sebanyak 0.1kg hingga 0.4kg dengan selang sebanyak 0.1kg setiap satu. Kesan ke atas permukaan setiap sampel selepas proses haus dan geseran dianalisis dengan menggunakan mikroskop optik. Salutan nanosilika kelihatan seragam dan berterusan kerana tidak menunjukkan sebarang gumpalan berlaku. Kandungan 3.0% nanosilika ke dalam PU yang lebih rendah dan optimum menghasilkan geseran dan kehausan yang rendah apabila beban dan kelajuan meningkat.

**Kata kunci :** Poliuretana berasaskan akrilik, salutan nanosilika, kelakuan haus dan geseran

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# CHAPTER 1

## INTRODUCTION

### 1.1 Introduction

Nanocomposites are polymers containing nanofillers, provide the microstructure that has inhomogeneities in the scale range of nanometers. Fillers of polymers have been used for a long time with the goal of enhanced performance of polymers, and especially of rubber. Polymer–clay nanocomposites were reported in the literature as early as 1961 (Zhou et al. 2002). Nanocomposites demonstrate often unusual and beneficial for the user properties. During past few years, use of silica and silicate nanofillers on epoxy coatings have been reported, it is widely used because of high performance nanocomposite, which consists of the incorporation of a nanometer-sized inorganic component into the organic resin matrix (Pascal et al.).

Acrylic based polyurethane was widely used as the high-quality auto-clear coatings. In recent years, much better properties of acrylic based polyurethane, such as better scratch resistance and weather ability, are desirable for the strong competitive market. Zhou et al. 2002 indicate that addition of nano-silica can improve the hardness, abrasion resistance, scratch resistance, tensile strength, modulus and weatherability of the polymer film. This study was mainly focused on the acrylic based polyurethane coating embedded by nanosilica.

For all nanocomposites, the interfacial area between the matrix polymer and nanoparticles is tremendously increased as compared to microcomposites and can be identified as one of the primary reasons for the altered materials behaviour. These considerations highlight the pronounced impact of nanoparticles on the surrounding polymer. For example, by dispersing 2 vol% of spherical nanoparticles (diameter 10nm) in a polymer matrix (interfacial thickness 10nm), the volume fraction occupied by the interfacial region is 52%, which implies that more than half of the composite is affected by the presence of nanoparticles. Besides the unique properties of nanocomposites provided by aforementioned structural features, a good dispersion as well as distribution of nanoparticles is a first priority.

In 2007, Chattopadhyay et al. published a study that related with the development of low-cost polyether polyols, PU coatings opened the door for automotive applications. Formulations and processing techniques continuously developed as one- and two-pack systems were developed. Today, PU coatings can be found on many different materials, to improve their appearance and lifespan. On automobiles, PU coatings give the demanded exterior high gloss, improved color retention, improved scratch and corrosion resistance. Different types of PU coatings are used in construction, where building floors, steel trusses and concrete supports are spray coated to make them more durable against environmental deterioration and less costly to maintain.

Depending on the polymeric matrix, the nanoparticle and its size in particular, optimum content of additive is in range of 1-4vol% for most system. When comparing the effects of nanoparticles and microscale additives on the wear behaviour of polymers, some main advantages of adding nanoadditives can be pointed out:

- (a) generally lower abrasiveness due to a reduced angularity
- (b) reinforcing effects possible, i.e enhanced strength, modulus and toughness
- (c) higher specific surface areas and, thus improved adhesion
- (d) in general, high effectiveness at very low contents

Gradual replacement of metal parts into polymeric components takes place in several industries especially in automotive and aerospace manufacture. Thus, the need for understanding the tribological behaviour of polymers is important since polymer matrix composites (PMCs) are subjected to abrasive wear in so many applications especially when plowing effect by counterface hard asperities that results in material removal and grooves like occur in coal handling and mining process.

Tribology is inherently complex with no governing laws for dry sliding friction or wear, and the state of the art in polymeric nanocomposites. Tribology includes many qualitative descriptors of important system parameters, such as particle dispersion, bulk mechanical properties, debris morphology, and transfer film adhesion, morphology, composition, and chemistry. Polymer tribology, as a research field, is now well-mature given that roughly 50 plus years have been publication of numerous research articles and reports dealing with a variety of tribological phenomena on a considerably large number of polymers, in bulk composite and hybrid forms. Tribological applications on polymers includes gears, a range of bearings, bearing cages, artificial human joint bearing surfaces, bearing materials for space applications including coatings, tires,

automobile brake pads, non stick frying pans, floorings and various types of surfaces for optimum tactile properties such as fibers and the list is still growing.

The use of nano-particles in polymers for tribology performance enhancement started around mid-1990s and this area has become quite promising for the future as newer nanomaterials are being economically and routinely fabricated. In the most cases, a polymer nanocomposite relies for its better mechanical properties on the extremely high interface area between the filler (nano-particles or nano-fibres) and the matrix (a polymer). High interface leads to a better bonding between the two phases and hence better strength and toughness properties over unfilled polymer or traditional polymer composites.

## **1.2 Objectives of study**

This research is carried out to study the tribological behaviour of nanosilica-PU coating. It is expected that this study will be helpful towards better understanding of the role of nanosilica in improving tribological behaviours of PU coatings. In order to promote this effort, the interest of the study includes:

- i) Analysis of the wear and friction behaviours of the nanosilica-filled polyurethane (PU) coatings on polypropylene (PP) substrate.
- ii) Study the influences of load and speed on the abrasive wear properties of the nanosilica-filled PU coating composite itself and the nanosilica-filled PU coating on the polypropylene (PP) substrate.
- iii) Investigation of the related wear and friction mechanisms based on the morphologies of the worn surface.



## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 Introduction

More recently there has emerged a new technology based on the formation of a nano-phase structure, consisting of small rigid particles or fibres with a diameter (or at least one dimension) of less than 100 nm dispersed in epoxy matrixes, which holds a great promise for increasing the mechanical performance of epoxies without compromising other desirable mechanical and thermal properties of the modified systems. The desired properties include enhancements in stiffness, toughness, UV absorption, flame resistance, [ionic](#)

[conductivity](#)

and [biodegradability](#). For example, incorporating metal-oxide nanoparticles such as nano-alumina and nano-silica into polymer coatings to enhance the mechanical durability has become widely utilized in the current anti scratch and mar technologies (Sung et al., 2008). The abrasion and scratching resistance of UV- cured coatings was greatly improved by incorporation into the polymer matrix of acrylate functionalized silica particles.

## **2.2 Role of nano silica addition**

One of the goals of nano-composite coatings is the production of coatings with enhanced properties such as higher micro hardness and corrosion and wear resistance (Aruna, 2009). Properties improvement of nanocomposite can be found, even at very low nanofiller content. From the recent research study in nanoparticle field, nanosilica particles have been widely introduced into polymers to improve the heat resistance, radiation resistance, and mechanical and electrical properties of the polymer materials. It has been clear stated from Zhou et al. in 2005, they found that nanosilica particles could more effectively improve the hardness, abrasion resistance, and scratch resistance, tensile strength, modulus and weather-ability of acrylic-based polyurethane coats than microsilica particles. Microsilica can only improve the abrasion resistance and hardness. Manna et al. 2008 found that the storage modulus and Tg of epoxidized natural rubber increased through addition of silica.

Furthermore, Wang et al. in year 2010 indicated that nanosilica particles could simultaneously provide PP with stiffening, strengthening, and toughening effects at rather lower filler content (typically 0.5% by volume). Addition of nanosilica particles to polyurethane acrylate coating is a simple and inexpensive method resulting in phenomenal increase in properties. Many great methods have been reported for the preparation of silica nanoparticles, such as plasma synthesis, chemical vapor deposition (CVD), sol-gel process, chemical precipitation method, microemulsion processing, combustion in diffusion flame and pressurized carbonation.

Due to their distinct feature as easy preparation, well defined dimensions and functional properties, Luo et al. reported that silica nanoparticles have occupied a prominent position in nanoscience. Thus, it presents a wide range of applications including catalysts support, pigments, chemo-mechanical polishing (CMP), hybrid composite materials, humidity sensors, electronic and thermal insulators. Moreover, Silica has been used in various industries for its electrical insulation, abrasion resistance and high thermal stability that is widely available in range of hydrophilic and hydrophobic forms. It is typically used in extremely fine particle size. Ultrasonic dispersing helps to use the potential of silica by improving the dispersion quality but typically silica is not well dispersed after wetting. It also adds a lot of micro bubbles to the product formulation (Kuldiloke 2002; Vaia et al 1993). The most important thing in silica application is having a good and uniform dispersion. Most research had studied that the basic challenge of nanocoating processing is because of dispersion technique. Due to strong adhesive force, nanoparticles tends to stick together and so as to form agglomerates or clusters in matrices, results in good mechanical properties and transperence degradation.

Particularly, in application of coatings and lacquers that to improve the scratch resistance, in order to avoid haze and maintain transparency, the particle size of silica have to be small enough not to interfere with the visible light to it. To fulfil this requirement, silica needs to be smaller than 40 nm for most coatings and for some other applications, particle agglomeration hinders each individual silica particle to interact with the surrounding media. Ultrasonic processing has been proven to be more effective in the dispersing of silica than other high-shear mixing methods.

### **2.3 Application of nanosilica coating**

There are many researchers who study about the applications of monodisperse silica particles ( $\text{SiO}_2$ ) that are now rapidly increasing, not only in the scientific field, but also in the commercial industrial fields. Advantages of  $\text{SiO}_2$  particles are currently used mostly by chemical and pharmaceutical industry (controlled drug release), biological sciences and industry of advanced and high-tech materials.  $\text{SiO}_2$  coatings also influence material's functionality, activity or can enhance its stability.

Conventional method of improving mechanical of coatings are based on enhancing the degree of cross-linking in the film and can be achieved by altering the nature of the resin, choice of the cross-linker, the catalyst and stoichiometric ratio. The higher the cross linking density, the higher the hardness and results in much better scratch resistance. When it subjected to nanoparticle coating, the presents of nanoparticle in surface layer of film enhance the scratch hardness and hence protect the film against marring, crocking, wearing and mild abrasions. The coatings are thus able to retain their gloss longer under the real life service conditions for automotives, wood furniture, parquet flooring and UV cured lacquers. The nanoparticles speciality is that they do not scatter light and become transparent like the clear resin film. When the particle size is in the conventional micron range, these metal oxides have a mattening effect on the coatings due to the scattering of light. When these particles is in nanoscale of 20-40 nm, they do not scatter light and become transparent like the clear resin film. Main contribution from nanosize is transparency to the visible light which helps retain

the film clarity. Even silica is not as quite hard as alumina but has lower refractive index closer to the resins and thus preserves the transparency better than alumina.

Organic coatings or paints on a substrate give aesthetic appearance as well as protection from the destructive phenomenon known as corrosion. Coatings can provide materials with the desired aesthetical properties such as color and gloss, but are of vital importance in the protection against environmental influences, including moisture, radiation, biological deterioration or damage from mechanical or chemical origin. This applies to both interior and exterior applications. The effectiveness of protection of a substrate against natural deterioration depends on factors such as the quality of the coating, the substrate characteristics, the properties of the coating/substrate interface, and the corrosiveness of the environment.

As plastics and plastic composites are placed into service in more demanding applications, surface modifications are performed to enhance the durability and increase service life. To date, part of the goals of nano-composite coatings is the production of coatings that can enhance properties such as higher micro hardness and corrosion and wear resistance. The hardening of the coating surface was induced by the presence of nano silica particles. Commonly, hard coatings are used on display screens to prevent damage; for example, coatings are applied to cellular telephone display screens to prevent scratching while the phone is placed in a pocket with keys and other sharp objects. (Agilent Technologies, 2010).

In research by Zhou et al. in 2005, they have studied the effect of nanosilica on the surface and interface, mechanical and optical properties of acrylic based polyurethane films. To do the comparison based on the coatings containing nanosilica,

the coatings with fumed silica and micro silica embedded were investigated. With the addition of nanosilica, results showed that microhardness, macro hardness, abrasion resistance, and scratch resistance were apparently improved. Furthermore, the tensile strength and Young's Modulus and UV absorbance in the wavelength of 290 – 400 nm were also improved with the increasing content of nano silica. However, only the elongation at break was decrease with the increasing of nanosilica content.

From an article by Song et al, in 2008, the colloidal nano-silica particles were used to improve the scratch and mar resistance of waterborne epoxy coatings by directly blending. In research by Mir et al. in 2011, in order to enhancing the compatibility of nano-silica particles within polymer matrix, nano-silica particles were first modified with 3-glycidoxypropyl-trimethoxysilane (GPTMS). The main reason that influences the excellent physical properties would be the high surface area/particle size ratio of nano-SiO<sub>2</sub>. Owing to the microstructure slippage, realignment and motion of polymer chains can be greatly obstructed. As a result, creep resistance of the PP based nanocomposites becomes much superior to those of untreated nano-SiO<sub>2</sub>/PP and also the unfilled version (Zhou et al., 2007).

The favourite nanoparticles for scratch and abrasion resistant coatings are silica and alumina. Nano-sized silica and alumina fillers appear to produce clear coats with similar surface hardness, UV-cured acrylate coatings reinforced by silica nanoparticles and corundum microparticles exhibit markedly improved scratch and abrasion resistance. Compared to nanocomposite materials, a much better abrasion resistance was obtained for coatings containing both silica nanoparticles and corundum microparticles. Nano/microhybrid composites are recommended as clear coats for parquet and flooring applications (Frank Bauer et al., 2007). Since the need for industrial heavy duty

floorings are increasing, Mir et al. 2012 had apply homogeneized SiO<sub>2</sub> nano particles with sonification mixing process in epoxy flooring formulation as a reinforcing agent which would result in high performance which applicable in different industries and results in excellent physical properties because of high surface area/particle size ratio of nano-SiO<sub>2</sub>.

In research conducted by Zhang et al. 2008, the well known basic challenge in nanocoating processing is the dispersion technique. Due to strong adhesive force and high surface energy, SiO<sub>2</sub> nanoparticles tend to stick together to form agglomerates or clusters in matrices, difficult to disperse uniformly into polymer matrix, consequently results in mechanical property and transparence degradation. Results shows that agglomerate free acrylate based nanocoatings were successfully prepared via a special sol-gel method and even at 40 wt% nanosilica particle content, all nanocoating samples showed high visible light transmittance and some ultraviolet screening effects.

To enhance the optimal utilization of natural resources and renewable resources, the interest is in growing towards the new material and the development of nanoparticle reinforced plastics. Based on research in India in 2010 by Lingaraju et al., the studied is based on the effects of nanoparticles as fillers in glass-epoxy composite system on mechanical and tribological studies. The sliding velocity and applied load have influence the wear process and effects the worn surface because the low load and speed combination make the matric tends to adhere to nanoparticles and give the lesser degree of debris formation. It was also found that the mechanical properties of the fiber reinforced composite show improvement with the inclusion of nanoparticles. The parameter used in this research is the wear test pin and flat surface in contact with rotating steel disc with the sliding speed of 640-1000 rpm, loads varies from 5-25 N and

time of 300-900 s respectively. The results showed that the wear rate increases with the increasing of the applied load, time and the sliding speeds.

## 2.4 Polyurethane (PU)

Otto Bayer and coworkers at I.G. Farbenindustrie, Germany in 1937 were the first to discover PUs in response to the competitive challenge arising from Carother's work on polyamides, or nylons, at E.I. DuPont (Chattopadhyay et al. 2007). Polyurethane (PU) has been used in many fields due to its excellent physical properties, such as abrasion resistance, elasticity, flexibility at low temperature and high waterproof. By taking the data from Gallagher Corporation that is a Charter Member of the Polyurethane Manufacturers Association (PMA), Polyurethane (or "urethane") elastomers are one type of a large family of elastic polymers called rubber. Urethanes have many advantages over metals, plastics and conventional rubbers that shows in Table 2.1 :

Table 2.1 : Advantages of polyurethane over metals, plastics and conventional rubbers

<b>Urethane vs. Metal</b>	<b>Urethane vs. Plastics</b>	<b>Urethane vs. Rubber</b>
Lightweight	High Impact Resistance	High Abrasion Resistance
Noise Reduction	Elastic Memory	High Cut & Tear
Abrasion Resistance	Abrasion Resistance	Resistance
Less Expensive Fabrication	Noise Reduction	Superior Load Bearing
Corrosion Resistance	Variable Coefficient of	Capacity
Resilience	Friction	Thick Section Molding
Impact Resistance	Resilience	Without a Cutting Gradient
Flexibility	Thick Section Molding	Colorability
Easily Moldable	Lower Cost Tooling	Oil Resistance
Non-Conductive	Low Temperature	Ozone Resistance
Non-Sparking	Resistance	Radiation Resistance
Often Lower Cost	Resistance to Cold Flow	Broader Hardness Range



	(or Compression Set) Radiation Resistance	Castable Nature Lower Cost, Low Pressure Tooling
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Polyurethanes are widely used in the mining industry because of their moderate cost, excellent mechanical properties and high wear resistance compared with alternative polymeric systems (Hill et al. 1997). Since polyurethane (PUR) elastomers possess great comprehensive properties in terms of high wear-, oil- and corrosion resistance, good adhesion to other materials and high elasticity and damping, it has been generally used in the industry and consumer products with heavy pressure, load, impact and wear (Fu et al. 2011).

Like for example, PURs are being used as wear-resistant materials to replace traditional metallic materials in the mineral and mechanical industries. However, there are still some disadvantages as using PURs as wear resistant materials because of their poor heat resistance, high costs and etc. In general, the temperature window of conditions within which PURs can be used as wear-resistant materials stretches from the glass–rubber transition (–50 to 25 °C) to tens of degrees below the melting or decomposition temperature (120 °C). The composites technology, in which particulate fillers are added into the polymers, may provide a good method for PUR to solve the above-mentioned problems (Zhou et al. 2002;2005).

However, PU has defects of low mechanical strength and low thermal stability for using in some specific areas. Most researchers are now focus and give wide attention on studying its synthesis, morphology, chemical and mechanical properties. Regarding to Gao et al. 2011, polyurethane (PU) is one of the most interesting synthetic materials in industry and most researchers nowadays interest to extend the application fields of

PU and start to search for higher performance of PU. It has been well known that polymer based nanocomposites exhibit remarkable improvements in mechanical, dielectric magnetic, thermal optical and acoustic properties compared with pure organic polymers. Furthermore, there have been some studies on the interfacial interactions between fillers and polymer matrix. Therefore, incorporation of nanoparticles into PU is a promising approach to improve its properties.

For PU coating classification based on Chattopadhyay et al. 2007, ASTM has grouped six different PU coating types in the ASTM D16 Standard that has been summarizes in Table 2.2. Most high solids and solventless PU coatings for high performance application and corrosion protection are designed using the plural component format of the ASTM D16-type V.

Table 2.2 : Different types of coatings by ASTM classification

ASTM Description	Characteristics	Curing mechanism	Polymer
Type I one-package (pre-reacted)	Unsaturated drying oil modified; no free isocyanate	Oxidation of drying oil; solvent evaporation	Alcoholysis products of drying oil; solvent evaporation
Type II one-package (moisture cured)	Contains free isocyanate	Reaction with atmospheric moisture	Higher molecular weight diols and triols
Type III one-package (heat cured)	Blocked isocyanate	Thermal release of blocking agent and then reaction	Prepolymer forms an adduct with blocking agents
Type IV two-package (catalyst)	Isocyanate prepolymer and catalyst	Reaction of isocyanate with moisture and/or components in catalyst	Prepolymer similar to type II, but catalyst could contain polyol/amine
Type V two-package (polyol)	Part A: Isocyanate rich Part B: Polyols or amines	Reaction between Parts A and B: instant curing is possible	Relatively lower molecular weight
Type VI one-package (non-reactive lacquer)	Fully polymerized Pus dissolved in solvents	Solvent evaporation	Thermoplastic polymer with relatively high

			molecular weight
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In research by Elleuch et al. 2007, the thermoplastic polyurethane elastomers (TPU) were used in the form of capsules for application in textile industry handling. The analysis of static mechanical characteristics constitutes an interesting tool for understanding the tribological behavior of TPU in sliding contact. The studies was conducted by using indentation tests with spherical steel indenter that can determine the material characterization as elastic modulus and adhesion force ( $E, F_{ad}$ ) and evaluating viscoelastic behavior of TPU. Elleuch et al. 2007 choose the friction of steel-TPU test in order to quantify the monotonous and cyclic friction phenomena and the damage of TPU was characterized based on wear scar and wear particles after a short number of friction cycles. Close correlation between friction and wear have been confirmed from topography investigation of TPU damage and the analysis had confirmed a good wear resistance of the TPU at real pressure (0.5 MPa) even for high number of cycles.

## 2.5 Tribology study

Tribology is a science that deals with design, friction, wear and lubricating surfaces in relative motion (Friedrich et al., 1995). For industrial application, the coefficient of friction, the wear rate and mechanical loaded carrying capacity are the most acceptability in tribological loaded components. Vinson and Chou 1975, Biswas and Vijayan 1992 stated that polymer based composite materials are the ones employed in tribological applications since the increasing demand in terms on stability at higher loads, temperatures, better wear properties and lubrication.

The economic consequences of wear are widespread and pervasive; they involve not only the costs of replacement parts, but also the expenses involved in machine downtime, and lost production. A further significant factor can be the decreased efficiency of worn plant and equipment which can lead to both inferior performance and increased energy consumption. Song et al., 2008 investigated the influences of load on the abrasive wear properties of silica filled epoxy resin composites and demonstrated that the friction coefficient and the wear rate of silica filled epoxy composites were lower than those of the pure epoxy. Zhang et al., 2008 has been studied the reduction in wear resistance and friction coefficient when nanosilica and nanoalumina were incorporated into the epoxy matrix. Moreover, Mell et al., 2010 has studied the effects of fillers on the wear resistance of thermoplastic polymeric coatings and found that silica and dolomite filled polymeric coatings had a higher wear rate than an unfilled polymer.

However, polymer-matrix composites (PMCs) are subjected to abrasive wear in many applications, due to plowing by counterface hard asperities resulting in material removal and grooves. From Martini et al. 2009, polymer matrix coatings has low shear strength and good toughness, but particularly significance in reducing friction and wears as well as extending service life of facilities involving surface contact and relative motion that due to their better cost-effectiveness than bulk materials. Coal handling and mining process of PMCs or coated with PMC are the typical field example that enhance to abrasive wear.

With the development of nanophased materials in recent years, attempts were made to develop nanoparticulate filled polymer composites to improve the tribological performance of the matrices. Kang et al. 2012 has successfully improved the wear resistance of epoxy resin (EP) by using nanosilica surface-capped with epoxide was used as a filler and incorporated into EP matrix generating filled EP composite coatings and found that friction reducing ability and wear resistance of the nanosilica-filled EP matrix composite coating do not necessarily change synchronically with varying EP to nanosilica mass fraction. EP-SiO<sub>2</sub> coatings that has been doped with a proper amount of hydrophilic nanosilica shows lower friction coefficient than EP coating. However, the introduction of surface-capped nanosilica as the filler results in inconsistent change in the friction coefficient and wear rate of the filled EP-matrix composites and further study need to be done to achieve well balanced friction reducing and anti-wear abilities of the composite coatings for tribological applications.

Zhang et al. 2009 reported that even the higher concentration of nanosilica reached up to 40 wt% used, both short term (pencil scratch) and long term (fretting) wear resistance of the nanocoatings was dramatically improved with the increasing nanosilica content. Compared with pencil hardness and fretting test at 40wt% nanosilica content, the pencil hardness had the most improvement to three higher grades while the wear volume on fretting process was reduce by ~68 times, as compared to unfilled neat coating.

In polymeric coatings, the used of nanoparticles are more in upgrading the level of resistance to wear and friction. Despite of using nanosilica particles, the other nanoparticles properties such as TiO<sub>2</sub>, SiC, ZnO, ZrO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub> were also chosen to improve and obtain good tribological test. Researcher from China in 2008, Song et al. has studied the tribological behaviours of the phenolic composite coating filled with

modified nano-TiO<sub>2</sub>. Nano-TiO<sub>2</sub> particles were modified by trifluoroacetic acid that produced a thin organic shell on nanoparticles. The addition of smaller amount of TiO<sub>2</sub> or TF- TiO<sub>2</sub> can improve the friction-reduction and anti-wear abilities of phenolic coating, and TF- TiO<sub>2</sub> as a filler is superior to TiO<sub>2</sub> in terms of ability of decreasing the friction coefficient and wear rate of phenolic coating. TF- TiO<sub>2</sub> strengthen the structure of the phenolic coating and effectively reduce its adhesive and ploughing wear, and enhance the formation of transfer films with better quality on the counterpart steel surface.

With respect to wear mechanisms of nanoparticles, as proposed by other researchers, the involved of nanoparticles can enhanced mechanical performance (e.g. modulus, hardness and fracture toughness), the rolling effect between material pairs or can improved bonding between transfer film and metallic counterparts (Zhang et al. 2008). Wang et al. 2010 showed that the addition of nanoparticles such as Si<sub>3</sub>N<sub>4</sub>, SiO<sub>2</sub>, SiC, and ZrO<sub>2</sub> could effectively reduce the coefficient of friction (COF) and wear rate for PEEK-based nanocomposites.

Friction in actual applications is very difficult to predict because of :

- a) The wide range of surface combinations
- b) The wide range of lubrication possibilities
- c) The non-linear relationship between the contact pressure (P), the sliding speed (V) and the coefficient of friction ( $\mu$ d)
- d) The effect of any temperature rise due to frictional heating on the coefficient of friction ( $\mu$ d)

For plastics, this can be even more complicated because plastics do not always follow the classical laws of friction that apply because of the large plastic deformations that occur at the tips of the asperities. Plastics do not react in this way, and the larger range of elastic deformation means that the coefficient of friction is generally lower than for other materials under the same conditions as shown in Figure 2.1. It is therefore only possible to give indicative values for the coefficient of friction for plastics unless the specific application conditions have been tested.

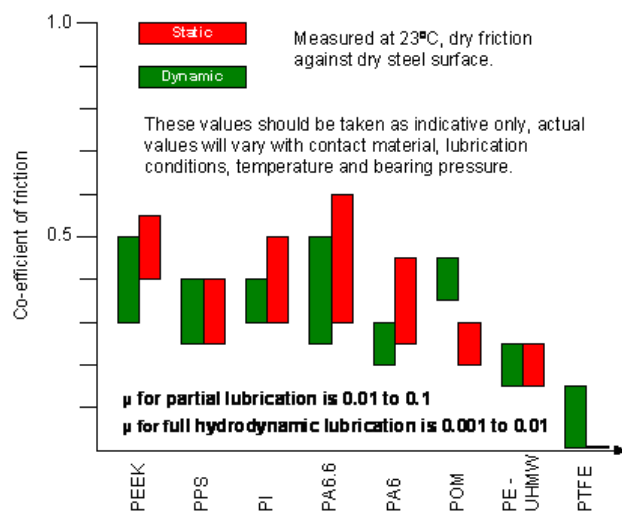


Figure 2.1 : Typical values for a variety of plastics against dry steel

The friction and wear performance of fabric reinforced composites is a complex phenomenon, which depends on the type of fabrics and matrices, volume fraction of the fibers, the fiber–matrix interfacial adhesion, the orientation of warp and weft fibers with respect to sliding direction, weaves of the fabrics, etc. Particularly, the effects of coating composition on the friction and wear behaviour of the composite coatings were highlighted in relation to their microstructure and worn surface morphology examined by means of scanning electron microscope.

In reality, there are no perfectly flat surfaces; there is always a degree of roughness because of asperities inherent to all surfaces; friction is due to the interaction between these asperities which results in energy dissipation. Wear is the direct result of the same processes that causes friction – the movement of the asperities on the surfaces over one another. If the frictional block and plate model is considered, then it is easy to see that the constant movement of the asperities over one another, with the repeated elastic and plastic deformation, will lead to material removal and a grinding down of the asperities. The model shown in Figure 2.2 is deliberately simple and would eventually lead to two smooth surfaces, in reality the removed material is trapped between the block and the plate and creates new grooves (and therefore new asperities) as the surfaces rub together.

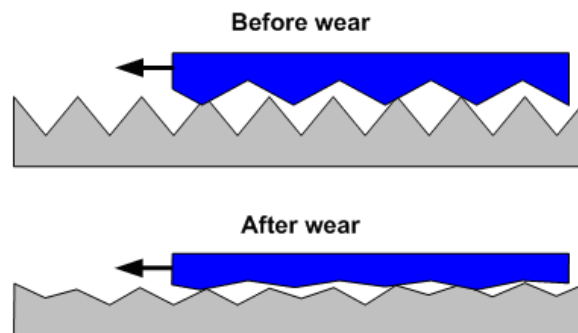


Figure 2.2 : The basic and typical understanding on wear



In research by Briscoe, he shows and simplified the approach of polymer wear classification seen in Figure 2.3. Wear mechanisms are classified under three broad approaches which reflect primarily the way this subject has been historically studied. It is demonstrated here that the wear of polymers is influenced by the contact conditions, the bulk mechanical properties of the polymer and the properties of the 'third body', which generally appears in the form of transfer film or degraded polymer particles between two sliding surfaces

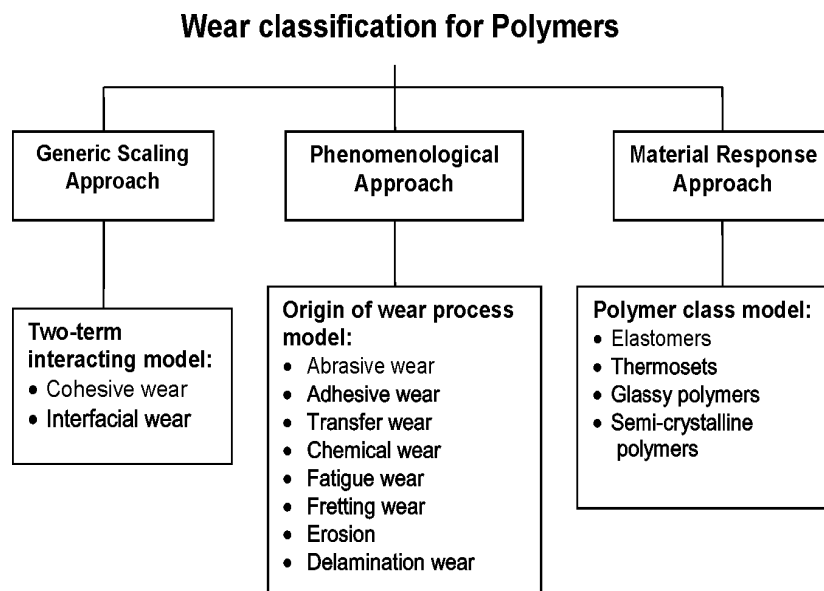


Figure 2.3 : Simplified approach to classification of the wear of polymers

## **2.6 Polypropylene (PP) substrate**

To introduce the substrate used, Polypropylene is the third polymer in the polyolefin family, first appeared in 1959, as a result of the development of stereospecific polymerization to obtain ordered polymers of a high degree of crystallinity. Polypropylene is an attractive engineering material due to its low cost, ease of processability, good mechanical properties, resistance to organic solvents, and favorable environmental aspects but the disadvantages of propylene are the lack of adhesion and poor scratch resistance (D. Feldman et al.). In research by M.H. Blees et al., they studied the adhesion of the sol gel coating on propylene by using scratch test method that focus on the effect of friction between indenter and coating on the critical load. The critical load (normal to the surface) showed a pronounced decrease of more than the order of magnitude with increasing friction coefficient. Comparing the results on the adhesion of sol-gel coating on the propylene that been induced by the microwave oxygen plasma modification is better than adhesion obtained by wet-chemical modification in chromo sulfuric acid at room temperature.

Polypropylene plate is often used for lining or complete manufacture of acid and chemical tanks and also sometimes used as back or chopping boards within the packing industry as it helps when the sharpened cutters penetrate the cardboard and acts as a substrate for the cutters edges. Polypropylene Sheet has two particular grades and they are Homopolymer grade Polypropylene and also copolymer grade Polypropylene. Homopolymer is a harder and more rigid grade that is available in natural and beige colour and has a larger range of size availability. Copolymer grade Polypropylene Sheet is more flexible and malleable, has better low temperature impact performance and is available in a much greater range of colours. Polypropylene Sheet is very light weight

and has a density of only  $0.91 \text{ g/cm}^3$  and is a plastic that actually floats and also can help with handling where large components are employed.

## CHAPTER 3

### RESEARCH METHODOLOGY

#### 3.1 Materials

In this work, acrylic based polyurethane, PU340 that has been primarily used in this study was supplied from Worldtex Specialty Chemical. Meanwhile nanosilica, Aerosil R972, that has been used for the preparation of the nanocomposites was supplied by Degussa Huls. This Aerosil R972 is one type of hydrophobic fumed silica treated with dimethyldichlorosilane (DDS) based on hydrophilic fumed silica. The average primary particle size of this Aerosil R972 was 16 nm in average diameter with the specific surface area of 130m<sup>2</sup>/g. The primer used was polyurethane resin in aqueous solution with the ratio acrylic base PU resin and solvent of 40/60 wt%. The solution was a mixture of toluene/isopropanol/ethyl acetate, work as a solvent in this study with a fixed ratio of 6:3:1. Propylene (PP) substrate with size of 110 mm x 25 mm x 1 mm was used as a substrate of the nanosilica/PU coating.

### **3.2 Preparation of Nano-SiO<sub>2</sub> filled PU composite coating**

Various amounts of nanosilica powders were added to the polyurethane (PU) resin so that the various compositions would turn out to be 3, 7 and 10% by weight respectively. The reference control was a pure polyurethane film without nanosilica content, noted as 0 wt% nanoSiO<sub>2</sub>-PU coating and used as comparative study. The mixtures were prepared by dispersing of nanoSiO<sub>2</sub> powder in solvent borne polyurethane under vigorously stirred using magnetic stirring at ambient temperature for at least 1 hour until clear dispersion and homogeneous mixture obtained. To obtain the same coating thickness for all samples, 1 g of the mixed suspensions were then directly coated on each polypropylene (PP) substrates using Rod Mayer technique that has been carried out in ambient temperature. Composition of nanosilica/PU system with 0-10 wt % nanosilica was prepared. Wire-wound rod with 0.5 inch in diameter and 12 inches in length was used to spread and disperse the nanocomposite materials on the surface of PP substrate as shown in Figure 3.1 and Figure 3.2. The wire-wound rod used has wire of 28 mils and the wet film thickness of 2 mils that will result after the coating passes through the grooves between the wires and hence get a uniform thickness on the substrates.



Figure 3.1 : Rod Mayer used in coating purpose

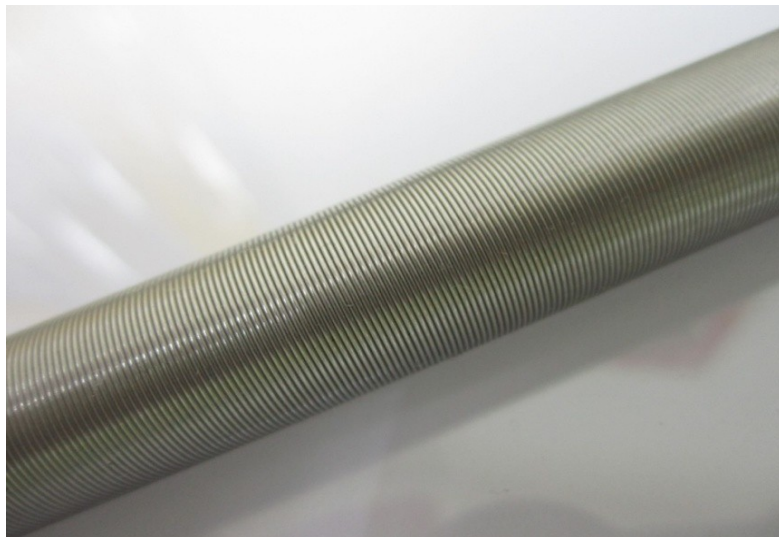


Figure 3.2 : Closed up of Rod Mayer used

### 3.3 Characterization

#### 3.3.1 Microstructure analysis of Nano-SiO<sub>2</sub> filled PU composite coatings

Various contents (wt%) of nanosilica that has been dispersed in PU were then coated on the petry dish and cured at room temperature (Figure 3.3). The thin coatings of nanoSiO<sub>2</sub>-filled PU were then carefully peeled off for characterization study. The microstructure of PU coating and nanosilica/PU composite coatings was examined with a Field Emission Scanning Electron Microscope (FESEM, Hitachi Corporation, Japan) with accelerating voltage of 0.8 kV. FESEM produces clearer, less electrostatically

distorted images with spatial resolution down to 112 nm that is suitable for conducting coatings on insulating materials and shows 3 to 6 times better than conventional Scanning Electron Microscope, SEM.



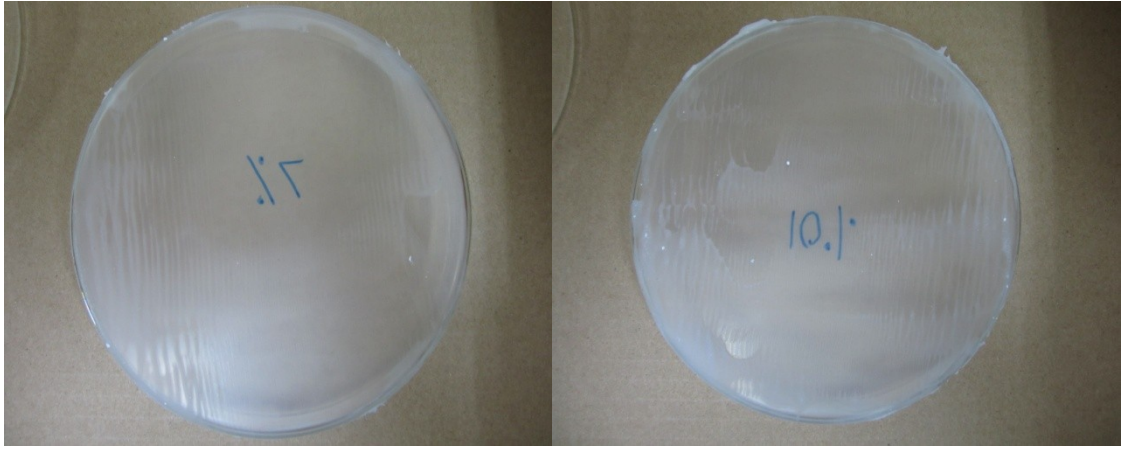


Figure 3.3 : Thin coatings of nanoSiO<sub>2</sub>-filled PU coated on petry dish

### 3.3.2 Wear and Friction test on PP substrate coated with nanoSiO<sub>2</sub>-filled PU composite coating

Friction and wear test method was used for determining the wear resistance of a pin of test material during sliding on the nanoSiO<sub>2</sub>-filled PU composite coating. The tribological tests were carried out by reciprocating sliding against steel in a pin on plate contact mode. The friction and wear test was conducted under a dry and clean condition using Reciprocating Wear Testing Machine (BICERI), Biceri Universal Wear Machine, serial no of WM1070/7 as can be seen in Figure 3.4. The schematic diagram of pin-on-plate contact mode of wear test shows in Figure 3.5. The sizes of samples used are 110 mm x 25 mm with the thickness of 2 mm. The sliding performs at rotary speed of 100 rpm and 200 rpm with the load varies from 0.1kg to 0.4kg with an interval of 0.1kg and duration time for 10 minutes. The reciprocal sliding tests were run at a sliding distance of 80mm/revolution. Before each test, the stainless steel pin was abraded with 900 grade water proof abrasive paper. Friction coefficient-time plots were automatically recorded by the test rig.



The worn surface after testing then was being observed using light optical microscope, Somecech Icamscope Light Source as shown in Figure 3.7. Wear rate values for both the pin and sample may also be calculated from the volume of material lost during a specific friction run (Song et al. 2008). The wear volume loss,  $V$  of the specimen was calculated from the relationship as below:

$$V = B \pi r^2 \left[ 1 - \sqrt{1 - \frac{b^2}{r^2}} \right] \quad (1.1)$$

where  $V$  is the wear volume loss ( $\text{m}^3$ ),  $B$  is the width of the specimen (m),  $r$  is the radius of pin (m), and  $b$  is the width of the wear scar (m). The wear rate ( $\omega$ ) was obtained from dividing the wear volume loss by the applied load (N) and  $L$  is the sliding distance (m).

$$\omega = \frac{V}{N \times L} \quad (\text{m}^3 \text{ N}^{-1} \text{ m}^{-1}) \quad (1.2)$$

All the friction and wear tests were carried out at ambient temperature, 20-25 °C with the relative humidity of 60%. A computer program periodically records the amount of

linear wear, which is equal to the decrease in pin height plus the depth of the groove worn in the plate.

Table 3.1: Parameters used for pin on plate test

Force Applied (kg)	0.1, 0.2, 0.3, 0.4
Speed of rotation (rpm)	100, 200
Duration of test	10 minutes
Density	7.8 g/cm <sup>3</sup>
Sliding Distance	80 mm/revolution
Contact area	6 mm <sup>2</sup>
Pin Material	Stainless steel
Pin Diameter	6mm





Figure 3.4 : Reciprocating Wear Testing Machine (BICERI), Biceri Universal Wear Machine

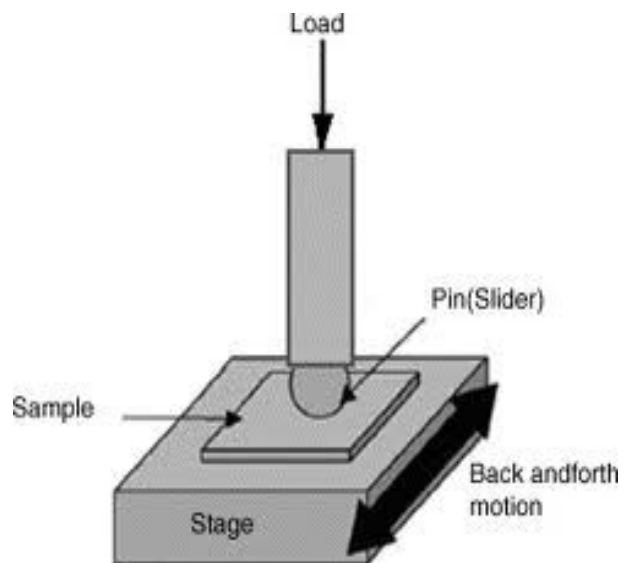


Figure 3.5 : Schematic diagram of pin on plate wear test

Load arm

Pin holder

Applied load



Figure 3.6 : Closed up on BICERI test rig



Figure 3.7 : Somecech Icamscope Light Source

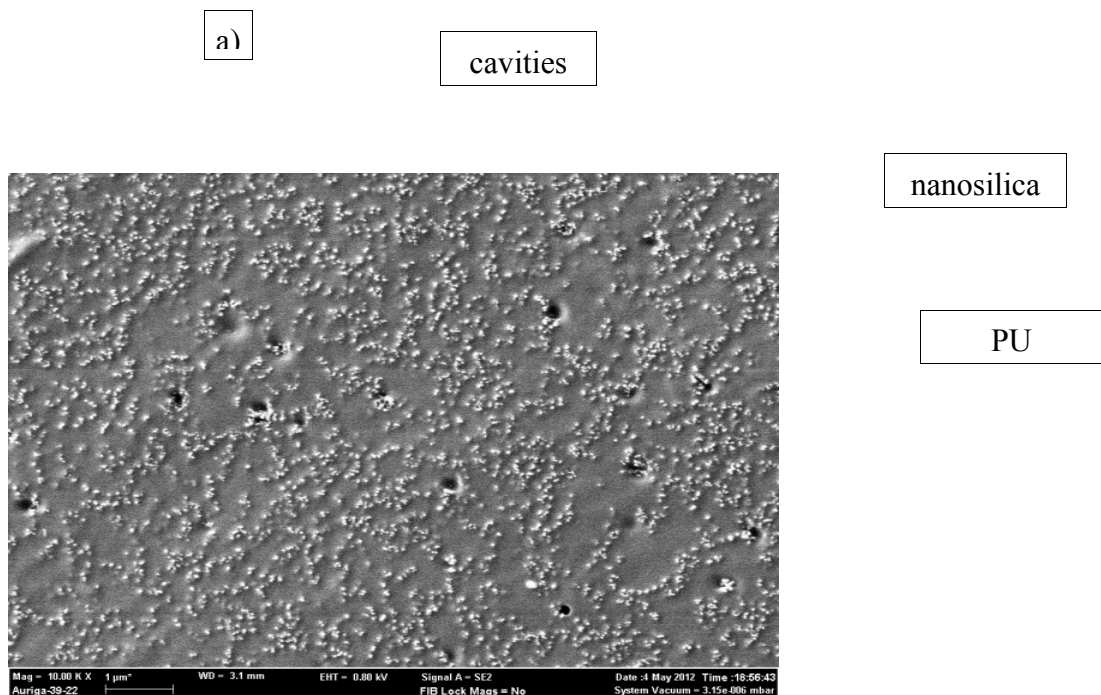
## CHAPTER 4

### RESULTS & DISCUSSION

#### 4.1 Microstructure analysis of nano-SiO<sub>2</sub>-filled PU composite coating

The dispersion of nanoparticles in the polymer matrix has been reported that having a significant effect on the mechanical properties of nanocomposite. The most critical and difficult way is in achieving a homogeneous dispersion since their tendency to agglomerate (Zhang et al. 2008). Homogeneity is the good reason that can conclude that the nanoparticles would fill the molecular cavities and providing better shaped

network. The composition of 7 wt% of nano-SiO<sub>2</sub>/PU coating was selected for being observed under FESEM micrographs to represent the particle distribution for other compositions as well. The thin coating of 7 wt% nanosilica/PU composite that has been done on the petry dish were carefully removed and being observed by using the Field Emission Scanning Electron Microscope (FESEM, Hitachi Corporation, Japan) with accelerating voltage of 0.8 kV. The FESEM micrographs in Figure 4.1 reveal that the nanosilica was dispersed homogeneously in polyurethane (PU) matrix.

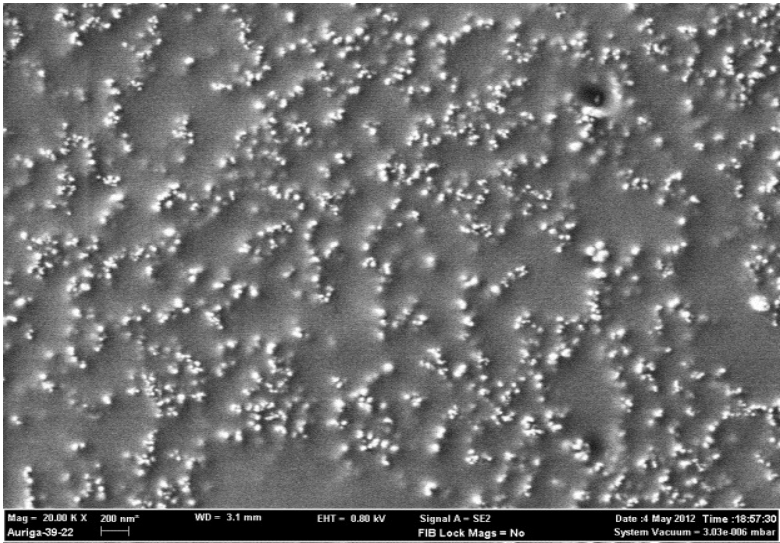


h

cavity

nanosilica

PU



c

nanosilica

PU

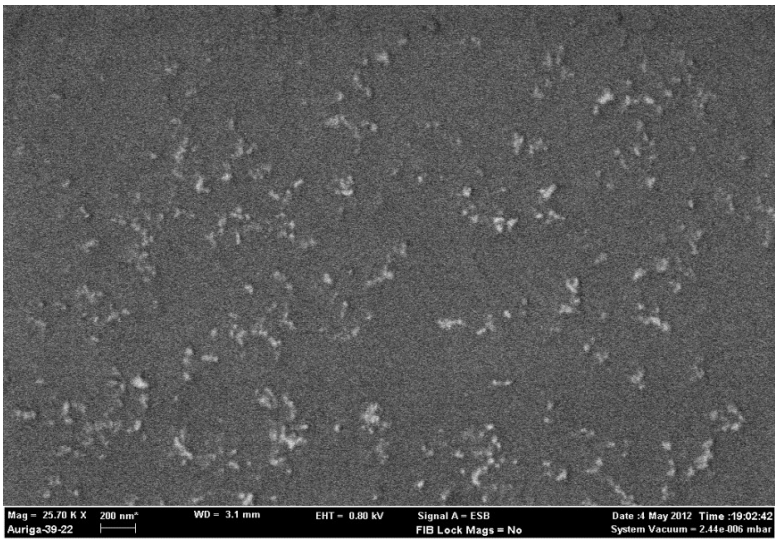


Figure 4.1 : FeSEM micrographs of ultra-thin section from coating samples filled with 7wt% of nanosilica : (a) magnification:10000X (b) magnification:20000X (c) backscattered image (BS), magnification : 25700X

The nanosilica particles used are around 16 nm in diameter with narrow distribution of particle size. For both lower and higher magnification in Figure 4.1 (a) and (b), there are no agglomerates can be found even at high nanoparticle contents up to 7wt% under magnetic stirring. The coating film seemed to be fine and homogeneous since no air bubbles generated in nanosilica-PU coating. This reflects the strong interaction and good miscibility between organic and inorganic constitutes, which are very beneficial to the improvements of various mechanical properties of the nanocoating. However, we found that there are some cavities or pores on the surfaces of nanosilica-PU coating that might be caused by the air bubbles trapped generated during the mixing and stirring process.

To confirm the image that being observe, backscattered image (Figure 4.1c) used to detect contrast between areas with different chemical compositions. The brighter image shows nanosilica particles and darker region is matrix of polyurethane since heavy elements (high atomic number) backscatter electrons more strongly than light elements (low atomic number), and thus appear brighter in the image.



## **4.2 Friction and wear behaviours of PP substrates coated with nanoSiO<sub>2</sub> filled PU coating**

### **4.2.1 Effect of nanoSiO<sub>2</sub>-filled PU composite coating on PP substrates on friction coefficient**

Figure 4.2 : The friction coefficient of nanoSiO<sub>2</sub> filled PU coated on PP substrates under load of 0.2kg and 0.4kg with speed 100 rpm in 10 min sliding time

Figure 4.2 shows the effect of nanosilica contents on the friction coefficient of nanoSiO<sub>2</sub> filled PU coating under load of 0.2kg and 0.4kg with the speed of 100rpm in 10 min sliding time. From this figure, compared to neat PU without the addition of nanosilica, we can see that at both 0.2kg and 0.4kg load, the unfilled nanosilica at 0 wt % shows the highest friction coefficient, 0.57 and 0.6 respectively. With increasing of nanosilica content up to 3.0 wt%, it shows the slight decrease in the coefficient of friction nanoSiO<sub>2</sub> filled PU coating. The introduction of lower content of 3.0 wt% of nanosilica into PU matrix gives the lowest friction coefficient at about 0.23. However, when the higher content of nanosilica introduced at 7.0 wt% and 10.0 wt%, the friction coefficient also increase for both 0.2kg and 0.4kg load. Hence, it can be concluded that the addition of small and optimum amount of nanosilica content can exhibit the improvement of friction coefficient of polyurethane coating.

Figure 4.3 : The friction coefficient of nanoSiO<sub>2</sub> filled PU coated on PP substrates under speed of 100 rpm in 10 min sliding time

In Figure 4.3, it shows the effect of applied load on the friction coefficient of nanoSiO<sub>2</sub> filled PU coating under the speed of 100 rpm in 10 min sliding time. It can be seen that the friction coefficient for all nanoSiO<sub>2</sub> filled PU coating increased with the increasing of applied load. At the same time, for 3.0wt % of nanoSiO<sub>2</sub> filled PU coating, it shows the lowest and smallest friction coefficient with increasing applied load up to 0.4kg, followed by 7.0 wt%, 0 wt% and 10wt% of nanosilica content respectively. The effect of load on friction coefficient can be explained by the elastic deformation of surface asperities under relatively lower load and the plastic deformation under relatively higher load, which was described by Kragelskii. Nanosilica filler aggregates on composite coating surface functions to resist abrasion by counterface asperities and hence can improve wear resistance of composite coating. This would result that at increasing friction coefficient with increasing applied load at higher load, the plastic deformation occurs at the asperities in contact. Increasing load after 3.0 wt%, more nanosilica dropped out from the polyurethane matrix during friction process, which led to severe abrasive wear and resulted in higher friction coefficient. However, nanosilica polyurethane coating assumed to be failed in many cases at higher applied load since it can lead to severe plastic deformation of polyurethane coating, owing to mechanical incompatibility between the coating and substrate.

Figure 4.4 : The friction coefficient of 3.0 wt% of nanoSiO<sub>2</sub> filled PU coated on PP substrates under speed of 100 rpm and 200 rpm in 10 min sliding time

Since 3.0 wt% of nanoSiO<sub>2</sub> filled PU composite coated on PP substrates shows the lowest friction coefficient, hence it appears as the optimal nanosilica content in PU. Then, this proportion was further investigated the effect in terms of applied load and speed on the friction and wear behaviours. As can be seen in Figure 4.4, it can be found that friction coefficient decreases up to 0.2kg load and then further increase with the increasing of applied load. Comparing the friction coefficient at speed 100 rpm and 200 rpm, when doubled the speed, the friction coefficient also increase with increasing of the applied load.

#### **4.2.2 Effect of nanoSiO<sub>2</sub>-filled PU composite coating on PP substrates on wear rate**

Figure 4.5 : Wear rate of nanoSiO<sub>2</sub> filled PU coated on PP substrates under load of 0.2kg and 0.4kg with speed 100 rpm in 10 min sliding time

In literature, general trends show that the friction and wear performance do not match each other. If friction behavior is good, wear performance is poor and vice versa. The effect on the nanosilica content on wear rate of polyurethane coating is clearly seen in Figure 4.5 at 0.2kg and 0.4kg applied load with speed of 100 rpm and sliding time of 10 mins. Compared to neat PU without the addition of nanosilica, at both 0.2kg and 0.4kg load, the unfilled nanosilica at 0 wt% shows the high wear rate and with increasing of nanosilica content up to 3.0 wt%, it shows the slight decrease in the value of wear rate of nanoSiO<sub>2</sub> filled PU coating. The introduction of lower content of 3.0 wt % of nanosilica into PU matrix gives the lowest wear rate, comparable to the introduction of 7.0 wt% nanosilica content that shows average wear rate value as 3.0 wt % of nanoSiO<sub>2</sub> filled PU composite coated on PP substrates. However, when the higher content of nanosilica introduced at 10.0 wt%, the wear rate also increase and give the highest wear rate for both 0.2kg and 0.4kg load. Hence, it can be concluded that the addition of small and optimum amount of nanosilica content can exhibit the improvement of wear rate of polyurethane coating.

Figure 4.6 : Wear rate of nanoSiO<sub>2</sub> filled PU coated on PP substrates under speed of 100 rpm in 10 min sliding time

The effect of applied load on the wear rate of nanoSiO<sub>2</sub> filled PU coating under the speed of 100 rpm in 10 min sliding time shown in Figure 4.6. From the graph, it can be seen that the wear rate for all nanoSiO<sub>2</sub> filled PU coating increased with the increasing of applied load. Same as the effect on friction coefficient, 3.0wt % of

nanoSiO<sub>2</sub> filled PU coating shows the lowest and smallest wear rate when load increase up to 0.4kg, followed by 7.0 wt%, 0 wt% and 10wt% of nanosilica content respectively. A higher content of nanosilica filler (e.g., 10wt %) means more severe aggregation of the filler thereby hindering the friction-reducing behavior of the filled composite coating, due to the abrasion action of the filler aggregates. On the other hand, nanosilica filler aggregates on composite coating surface may function to resist abrasion by the counterface asperities thereby resulting in improved wear resistance of the composite coating.

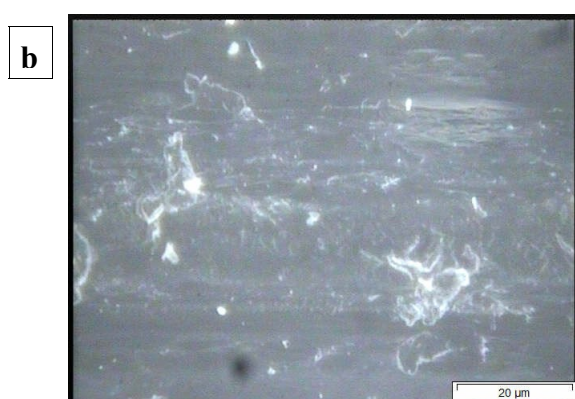
Figure 4.7 : Wear rate of 3.0 wt% nanoSiO<sub>2</sub> filled PU coated on PP substrates under speed of 100 rpm in 10 min sliding time

Since 3.0 wt% of nanoSiO<sub>2</sub> filled PU composite coated on PP substrates shows the lowest value of wear rate and hence selected as the optimal nanosilica content in PU. This proportion was further investigated the effect in terms of applied load and speed on the wear behaviours. In Figure 4.7, it has clearly shows that there was a tremendous increase of wear rate for both 100 rpm and 200 rpm with the increasing of applied load. This indicates that the addition of nanosilica helps in improving the ability of carrying load in the polyurethane (PU) coating. The better anti-wear behaviours of nanosilica coating under different applied loads mainly dominated by the elastic deformation of surface asperities under relatively lower load and plastic deformation under relatively higher load that has been described by Kragelskii. Hence, it can be concluded that the optimal amount of nanoSiO<sub>2</sub> is at 3.0 wt% filler aggregates on composite coating

surface may function to resist abrasion by the counterface asperities thereby resulting in improved wear resistance of the composite coating.

#### **4.3 Worn surface analysis of nano-SiO<sub>2</sub> filled PU coated on PP substrate after friction & wear test**

### 4.3.1 Effect of nanosilica contents on polyurethane (PU) coating



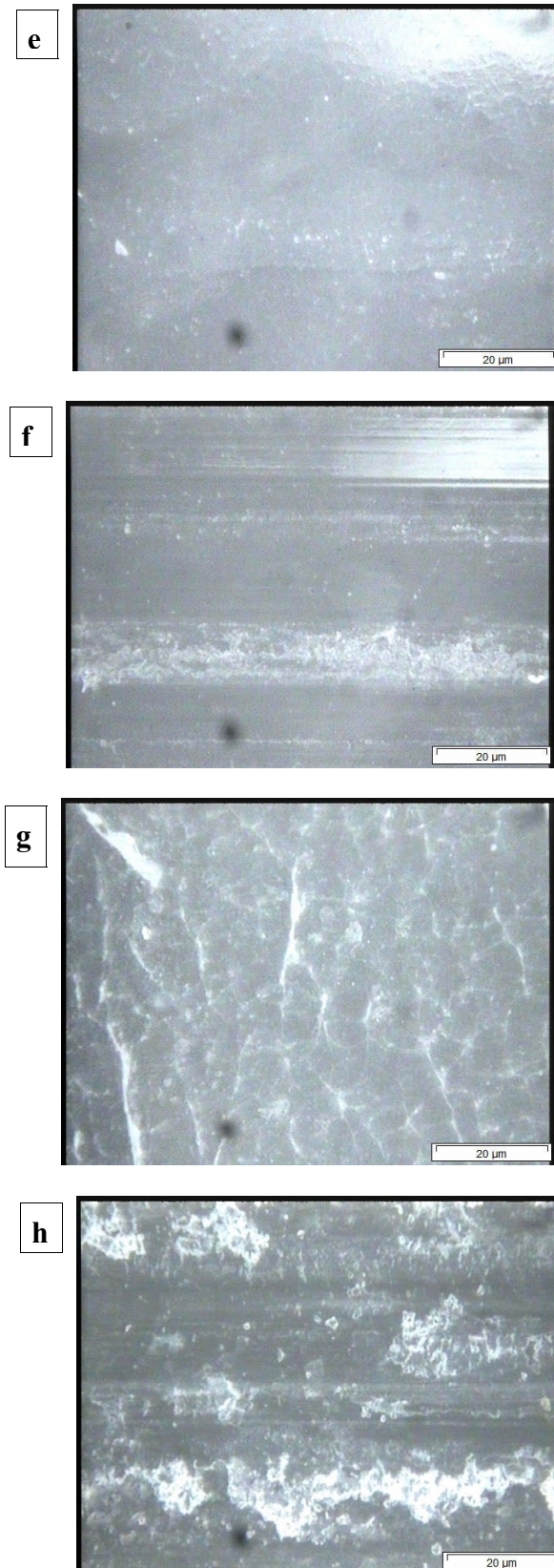


Figure 4.8 : Optical micrographs before and after worn on the surfaces of polyurethane coating filled with different nanosilica content (100rpm, 10 mins) magnification of 300x with:

- (a) 0wt% nano-SiO<sub>2</sub> before worn;    (b) 0wt% nano-SiO<sub>2</sub> after worn ;
- (c) 3wt% nano-SiO<sub>2</sub> before worn;    (d) 3wt% nano-SiO<sub>2</sub> after worn;
- (e) 7wt% nano-SiO<sub>2</sub> before worn;    (f) 7wt% nano-SiO<sub>2</sub> after worn;
- (g) 10wt% nano-SiO<sub>2</sub> before worn;    (h) 10wt% nano-SiO<sub>2</sub> after worn;



Figure 4.8 shows the optical micrographs before and after worn of polyurethane coating filled with different nanosilica content under dry sliding of pin on plate contact mode wear test with the magnification of 300X. The worn surface after wear test (see Figure 4.6b) of the unfilled nanosilica PU coating shows signs of adhesion and abrasive wear compared to the surface before worn (see Figure 4.6a). The corresponding surface is very rough, displaying plucked and ploughed marks indicative of adhesive wear and ploughing. This is might due to fatigue-delamination generated under repeated loading during sliding. Fatigue wear has been regarded as a main mechanism responsible for the sliding of the unfilled PU coating against a hard counterpart. This phenomenon corresponds to the relatively poorer wear resistance of the unfilled nanosilica in PU coating sliding against the steel.

For introduction of lower content of nanosilica (e.g 3.0 wt%), it can be seen that the worn surface were smooth and shows only fine scratches as shown in Figure 4.6(d) compare to surface before worn (see Figure 4.6c). This smooth, uniform and compact worn surface leads the good influenced in increasing the wear resistance of nano-SiO<sub>2</sub>-PU coating. The fractured surface was characterized by brittle fracture and little fiber pulling-out can be seen, which indicated that the addition of nano-SiO<sub>2</sub> improved the adhesion between the filler and matrix. As increase the nano-SiO<sub>2</sub> content, the worn surface appeared by severe plastic deformation and microcracking (refer Figure 4.6f and h) compare to smooth surface before the wear test (refer Figure 4.6e and g). Hence, it is

clear that the introduction of optimum amount of nanosilica exhibits strengthened and strong filler–matrix bonding which definitely played an important role in improving the tribological properties of the composites coating.

#### **4.3.2 Effect of applied load on nanoSiO<sub>2</sub> filled PU coating coated on PP substrate after friction & wear test**

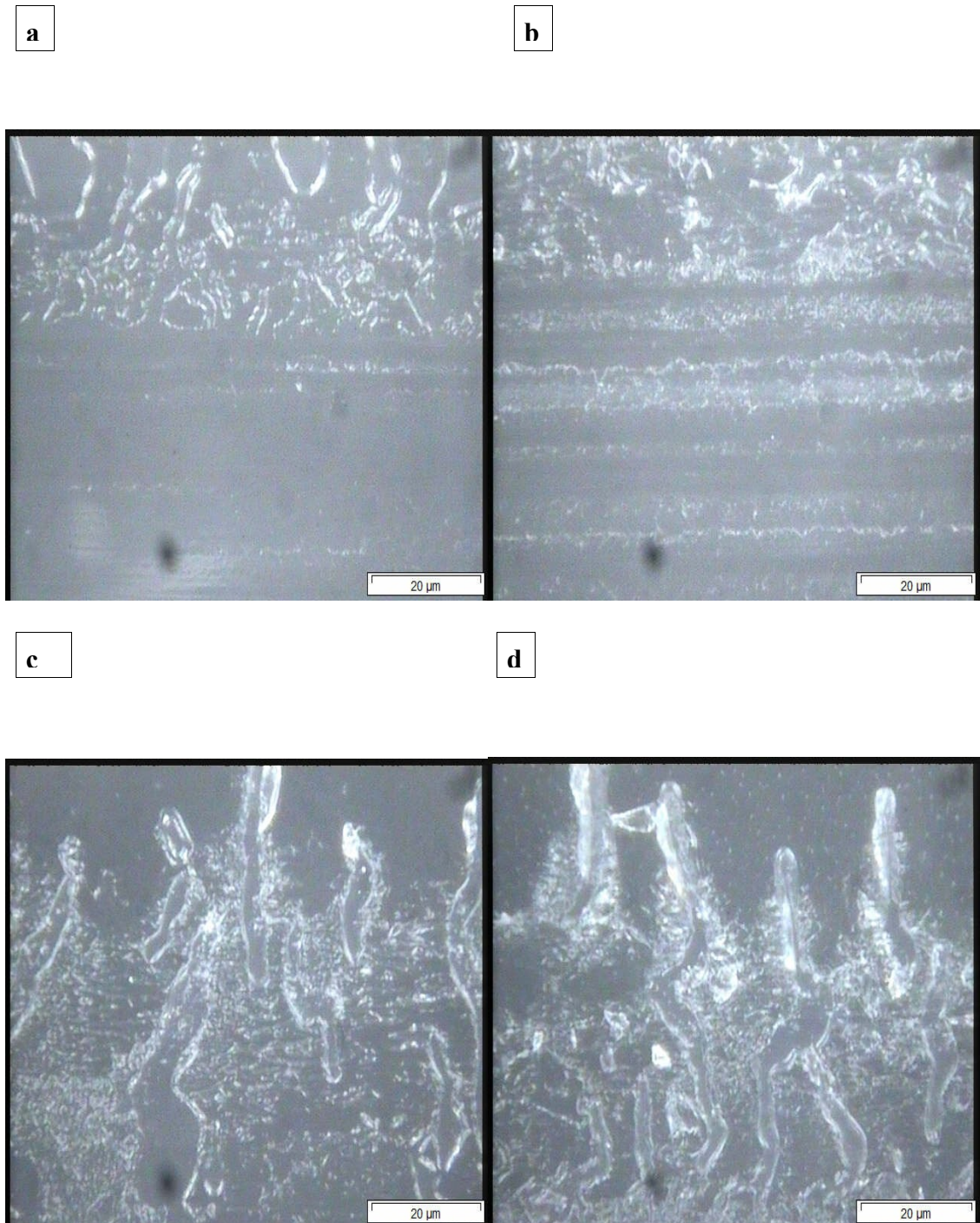


Figure 4.9 : Optical micrographs of the worn surfaces of 3wt% nanosilica filled polyurethane coating under different applied load, magnification of 300X, speed 100 rpm with load of:  
(a) 0.1 kg; (b) 0.2kg; (c) 0.3kg; (d) 0.4kg

For the best combination, the 3wt% of nano-SiO<sub>2</sub> was chose for further investigations of worn surface on the effect of applied load. The worn surfaces of 3.0wt % nanoSiO<sub>2</sub> filled PU coating are shown in Figure 4.9(a)-(d) under different applied load. At low load, it can be seen that the worn surface of the coatings were smooth under 0.1kg load with speed of 100rpm (see Figure 4.9a). When the applied load was increased at 0.2kg, there are some adhesion marks and cracks on the worn surfaces as shown in Figure 4.9(b). With further increase of applied load, (see Figure 4.9c and d), there are some large amount of cracks or flaky debris in the worn surface would be crushed or sheared into smaller particles or thinner flakes and acted as lubricants. At the same time, the newly formed debris would come into being a more integrated layer on the worn surface and reduced the ‘direct contact’ between the fabric composite and the counterpart.

#### 4.3.3 Effect of speed on nanoSiO<sub>2</sub> filled PU coated on PP substrates after after friction & wear test

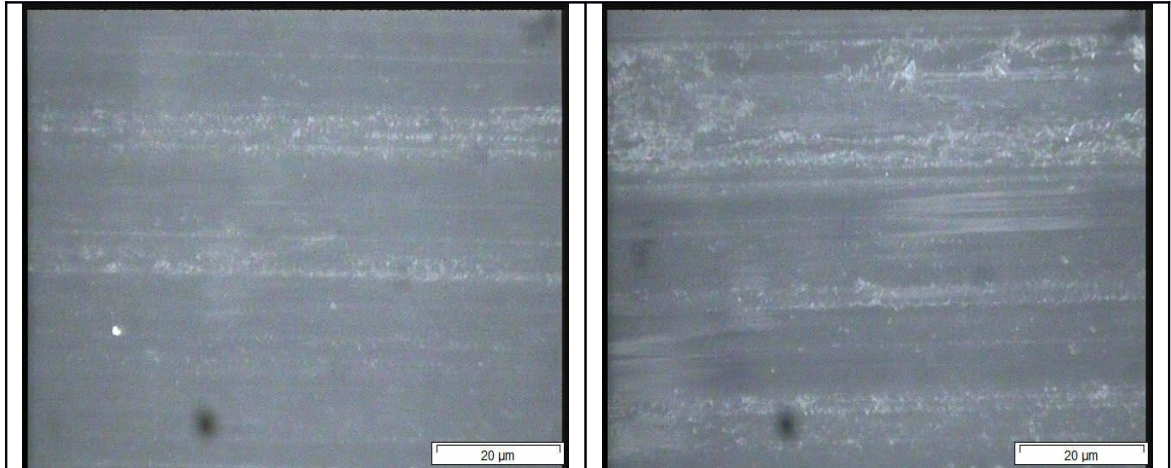


Figure 4.10 : Optical micrographs of the worn surfaces of 3wt% nanosilica filled polyurethane coating under 0.2kg load, magnification of 300X, with different speed of: (a) 100 rpm, (b) 200 rpm ;

The effect of speed on the worn surface of 3.0 wt% nanoSiO<sub>2</sub>-filled PU coated on PP substrates shown in Figure 4.10. In Figure 4.10(a) shows the worn surface with the speed on 100 rpm shows there are mild wear occur on the worn surface. In Figure 4.10(b), the wear become from mild to severe, which indicates that the serious fatigue wear is the main wear mechanism of the filled PU coating when sliding under higher speed. It can be inferred that large area of frictional surface of the filled PU coating would flake away if the speed increases further and the coating would be seriously damaged.

## CHAPTER 5

### CONCLUSION

#### 5.1 Conclusion

Based on the studied devoted to investigate the friction and wear behaviour of nanoSiO<sub>2</sub>-PU coating, the following discussions can be drawn:

Agglomeration-free of nano-SiO<sub>2</sub>-PU coating successfully obtained by using magnetic stirring. The coating film seemed to be continuous and homogeneous since no air bubbles generated in nanosilica-PU coating and reflects the strong interaction and good miscibility between organic and inorganic constitutes.

The friction and wear behavior of nanoSiO<sub>2</sub>-PU composite coating sliding against stainless steel pin-on-plate contact mode were closely related with the sliding condition, such as sliding speed and applied load. The addition of small and optimum amount of nanosilica content (3.0 wt%) can exhibit strengthened and strong filler–matrix bonding which definitely played an important role in improving the tribological properties of the composites coating.

For the best combination based on lowest friction coefficient and wear rate, 3.0 wt% is noted as optimum content of nanosilica since with a rise in applied load and speed, it still give the lower friction coefficient and wear rate compare to other nanosilica contents.

#### 5.2 Recommendation for Future Studies

Improvements in this study were critical to improve in producing better understanding based on tribological properties. There are still plenty of further research awaits to reach a compromise between the friction coefficient and wear resistance of nanoSiO<sub>2</sub>/PU coating on polypropylene substrate before they are put into practical tribological application. In order to have a better understanding, further studies are suggested below;

a) Morphologies of the worn surface analysis of polypropylene substrate coating and steel counterpart sliding pin to compare and characterize prior to and after the tribological test using SEM@ FESEM to ensure the clearer image of the effect of wear test on nanoSiO<sub>2</sub>-filled PU on polypropylene substrate, hence to make a better understanding on the tribological behaviour.

b) To study and develop a new or modified distribution techniques of nanosilica on polyurethane instead of Rod Mayer, like spray gun which results in positive improvement on the tribological properties of the nanoSiO<sub>2</sub>-filled PU.

c) Instead of wear scar diameter, the most convenient way to measure wear is in terms of weight loss or volume loss. The volume loss was determined using the formula suggested by ASTM G99 standard. For this, the wear track width was calculated by examining the wear tracks under SEM.

d) Measurement of coating thickness is important to understand its tribological performance. Normally coating thickness provides the barrier

between the environment and substrate. Moisture and corrosives which have significant influence on tribological behaviour are comparatively more impermeable to the thicker coating. Therefore, variation of tribological properties versus actual coating thickness needs to be taken into consideration.

e) Undergoing the test for 1, 2 and 4 wt% of nanosilica content to check the validity of the reported findings.

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